Site Need Statement

General Reference Information		
1 *	Need Title: Chemical and Physical Behavior of Sludge Wastes	
2 *	Need Code: RL-WT090	
3 *	Need Summary: Provide additional chemical, physical, and hydrodynamic information to guide the retrieval, delivery, and caustic leaching of Hanford tank sludge wastes.	
4 *	Origination Date: November 2000	
5 *	Need Type: Technology Need	
6	Operation Office: Office of River Protection (ORP)	
7	Geographic Site Name: Hanford Site	
8 *	Project: Retrieval PBS No.: RL-TW04	
9 *	National Priority: X1.	
10	Operations Office Priority: High	

Problem Description Information

- Operations Office Program Description: The overall purpose of the Retrieve and Transfer DST Waste function is to provide feed to the Waste Treatment Plant (WTP) and receive waste from SSTs. A primary objective of this function is to provide the tank farm infrastructure necessary to deliver waste to the WTP within established specifications. The baseline end state of the Retrieve and Transfer DST Waste function is:
 - Retrieval of all wastes from the DSTs
 - The safe, environmentally compliant transfer of this waste to the WTP
 - DSTs in a ready state for implementing closure and final disposal of the DST farms.

The overall purpose of the Retrieve and Transfer SST Waste function is to move the waste from the SSTs into preferred storage in the DST system. A primary objective of this function is to develop and test alternative and improved retrieval technologies to past-practice sluicing. As part of this effort Leak Detection Monitoring and Mitigation (LDMM) approaches are being developed for concurrent deployment. To support this effort Cold Test Training & Mock-up Facilities are being established. The baseline end state of the Retrieve and Transfer SST Waste function is:

- Retrieval of all wastes from the SSTs
- The safe, environmentally compliant transfer of this waste to the DSTs
- SSTs in a ready state for implementing closure and final disposal of the SST farms.
- Need/Problem Description: Wastes must be transported and treated with minimum cost and delay. To this end, the transfer and treatment equipment must be designed correctly, and the operating plans must be accurate. Successful design and operation both rely on accurate knowledge of the chemistry and physical properties of the wastes to be treated. Although a good deal of information has been obtained about the elemental composition of the waste, we do not yet have complete knowledge of the chemical compounds formed by these elements. Knowledge of the chemical compounds present in sludge wastes is important to predict the degree of completeness of caustic leaching and the manner in which leach rate and completeness are affected by variations in process parameters.

Needs related to leaching: Knowledge of the chemical compositions of the wastes by itself will provide

general indications of leachability and the effect of process parameters on leachability. However, to develop a reliable capability for quantitative prediction of leachability, this knowledge must be coupled with leach tests on actual waste samples. Such leach tests have already been performed on 30 samples of sludge, representing 75% of the total sludge volume at Hanford. Testing of another 17 samples would complete a plan to cover 93% of the sludge. Information is needed about the rate, as well as the total extent of dissolution that may be obtained under potential processing conditions. A special concern involves the REDOX-type sludge wastes, which contain most of the hard-to-remove chromium; these wastes require additional testing to confirm chromium removal efficiencies.

e kinetic information will also assist in designing and operating the leaching step most efficiently. Systematic evaluations of the effects of temperature, alkalinity, ionic strength and other parameters on the rates of dissolution and solid state phase transformations (such as interconversion of gibbsite to boehmite, or reactions rates involving sodium aluminate) are presently unavailable. Our present level of understanding of the behavior of chromium in the Hanford waste tanks is based only on observations at a few selected conditions for specific wastes. There are few available data on the equilibrium behavior of chromium compounds in tank-like environments, and kinetic information under these conditions is virtually nonexistent. Like aluminum, chromium dissolution in basic solutions is not an instantaneous process; preliminary unpublished data on the dissolution of chromium solids in high base suggests a significant decrease in solubility with time.

chromium system is complicated by its redox chemistry. The oxidation state of chromium in the waste is surmised only from its solubility behavior. Thus, systematic evaluation of the solubility and kinetics of chromium compounds must also cover the oxidation of Cr(III) to Cr(VI). Fundamental investigations of the equilibria and kinetics of reactions involving the Cr(III) – Cr(VI) transitions are necessary. The chemistry is likely to be strongly dependent on temperature, alkalinity and various other parameters. Thus, a systematic investigation of the general equilibria and dissolution/precipitation kinetics of chromium compounds in concentrated alkaline solutions is key to predicting the behavior and speciation of chromium in the Hanford tank systems.

Needs related to leach solution stability: Once chemical constituents have been leached from the waste, it must be ascertained that subsequent processing will not cause re-precipitation or gel formation. This question will be addressed mainly by the Environmental Simulation Program (ESP) chemical equilibrium software (OLI Systems, Inc., Morris Plains, NJ), but the applicability of this software for predicting the solubilities of chromium, aluminum, and other elements of concern in alkaline solutions of high ionic strength must be demonstrated by laboratory testing.

Needs related to physical properties of sludge: Information about the physical properties of sludge wastes is also incomplete. Knowledge of particle size distribution and particle density is required for the design of waste transfer systems (pipes and pumps) and to determine whether transfers of slurries can be completed as planned. Although some particle size distribution measurements have been made, the densities of the particles in the wastes are unknown. Furthermore, the role of particle agglomeration is only beginning to come to light; it is not known whether agglomerates will be broken up in pumps, nor whether disrupted agglomerates will re-form during pipeline transport. Basic information is needed about the effect of turbulence, ionic strength, temperature, and other processing variables on agglomeration. The information could also be used in the future to select tank cleanup methods, including for example high velocity fluid shear-based technologies.

Needs related to sludge transport: Additional work is advisable to determine the transportability characteristics of Hanford sludge wastes. The model use to estimate the required transport velocity and to predict the head pressure that will be developed has been adapted from other industries and has not been qualified on Hanford slurries. Tests to demonstrate the minimum required transport velocity for Hanford slurries would be beneficial. The transport model should be extended to incorporate theory associated with agglomeration and de-agglomeration.

Despite pipeline plugging over many years at Hanford, the technologies for removing plugs are still not well

developed. Although it should be possible, through adequate planning, to avoid plugging of lines during delivery of the wastes to the waste treatment plant, having reliable methods for removing sediments from pipelines can benefit the project by reducing the need for excessive conservatism. Additional and advanced technologies for unplugging pipelines should be demonstrated and characterized to improve overall project efficiency.

Problem Background: Solids and gels may form in the Hanford tank waste under certain processing conditions. Transfer lines have been plugged when solids or gels inadvertently formed. Knowledge of the solubility envelope for the waste is necessary to avoid unwanted precipitation or gel formation in supernatants. Improvements in processing efficiency are expected if the retrieval, pipeline delivery and treatment plant processes are based on an understanding of the dissolution thermodynamics and kinetics rather than just empirical data. Water use and makeup chemical addition can also be reduced which, together with the improvement in efficiency, can reduce the amount of HLW glass produced. Knowledge of waste solubility is necessary to avoid unwanted precipitation or gel formation in supernatants and to recover from such events should they occur.

The volume of the HLW fraction of the immobilized waste that is produced by the plant (i.e., the glass that must be stored in a deep geologic repository) would be driven to a large extent by the chromium and aluminum content of the waste feed, if they are not removed. If these two metals can be dissolved out of the primarily water-insoluble HLW feed, the volume of immobilized waste, and, therefore, the overall cost of the Project can be reduced substantially. The lack of adequate understanding of aluminum and chromium dissolution chemistry will lead to overly conservative (i.e. overly expensive) design of both the Phase 1 and Phase 2 plants.

Similar needs: Need RL-WT091 deals with parallel issues for retrieval, delivery, and treatment of salt-type wastes

Program Baseline Summary (PBS) No.: TW04

- ** Work Breakdown Structure (WBS) No.: 5.02.02.01.02.01
- TIP No.:

13 Functional Performance Requirements:

Requirements related to leaching: A fundamental understanding of aluminum and chromium chemistry, including identification of the compounds of those elements that are present, shall be developed to support prediction of the solubility of those elements in Hanford tank systems and under the currently planned inplant sludge washing conditions. The solubilities and dissolution rates of these components shall be quantified as functions of temperature, alkalinity, presence of oxidizers, etc. The test conditions shall match the planned process parameters, so that the relative efficiencies of various proposed removal strategies can be compared.

In order to compare leaching strategies effectively, solubility data for other components of interest in the sludges shall also be obtained. These data will be used in the ESP chemical equilibrium model.

During these studies, data shall also be obtained to determine the effect of the processes (especially oxidation processes for chromium removal) on organic complexants and solubilities of strontium and transuranic compounds.

Requirements related to leach solution stability:

bility information for the major species expected in leach solutions shall be compiled in a form suitable for inclusion in ESP. The compilation shall include problem species such as aluminate, silicate, and chromium species. The work shall include literature reviews to identify what solubility data are missing and identify what experimental work is needed to provide the missing data.

Requirements related to physical properties of sludge:

mation shall be obtained to demonstrate how the data obtained with a light-scattering particle size distribution instrument relates to the particle sizes actually present during transport of a slurry. Information

shall be obtained to estimate the density of waste slurry particles under transport conditions. A correlation shall be developed to yield critical velocity and pressure drop for slurries containing agglomerated solids. The inputs to the correlation shall be measurable, calculable, or known.

Requirements related to sludge transport: Full-scale tests shall be performed with simulants to identify and/or confirm potential problem conditions. Pump rates will be about 140 gpm through 3" diameter lines.

An empirical model (but with a strong foundation in theory) shall be developed to predict chemical adjustments required to support transport and settling operations. The model shall incorporate theory associated with agglomeration, sedimentation, and fluid dynamics. Dilution effects, including temperature reduction and solids dissolution/precipitation, shall also be included.

This model shall utilize waste composition and operating conditions as its inputs. It shall provide a technical basis for pipeline transport specifications; such basis is currently deficient and may be overrestrictive. The model shall include a means for predicting the formation of solids and gas during pipeline transfer, and the physical properties of these inhomogeneities, such as particle (and bubble) sizes, shapes, and densities, and the relation of these properties to foam stability and plug formation. The model shall demonstrate dependence of the particulate properties on hydrodynamic conditions and history; this information would lead to calculations of sedimentation rate and transfer design parameters, such as critical flow velocity and head pressure. This tool shall also be able to predict the effect of blending different chemical waste types.

** Schedule Requirements: Physical property information about sludge wastes will continue to have value as systems and operations are designed to remove wastes from single shell tanks. Time and dollars can be saved by knowing how to translate laboratory measurements of waste characteristics into predictions of retrieval efficiencies and other measures of operational performance.

hability information supports the SST retrieval sequence analysis. The retrieval sequence analysis will provide the foundation for Phase 2 planning, and meets Tri-Party Agreement Interim Milestones M-45-02D through M-45-02I (annual updates of the SST Retrieval Sequence document). Information about waste leachability obtained through FY04 may be incorporated in the equipment design and operating plans of the waste treatment plant.

All information developed in response to this site need will have use in improving process operations throughout the life of the project (>20 yr). However, information available before the treatment plant equipment design and processes are finalized will produce the largest cost savings. For the Phase 1 (pilot) facility, this is in the 0-to-2-year time frame; for Phase 2, this is in the 10-to-20-year range.

- Definition of Solution: This site need will have been met when the chemical and physical characteristics of Hanford's sludge wastes are known well enough that the costs for retrieving and delivering those wastes to the WTP can be predicted to within 20%.
- 15 * **Targeted Focus Area:** Tanks Focus Area (TFA)
- Potential Benefits: A significant cost avoidance is expected if line plugging or problems with flow capacity can be avoided. Plugs are expensive to remove or repair (~\$1M per occurrence), but more serious is the likelihood of plant downtimes of several weeks or months. Programmatic delays may cause violation of the Tri-Party Agreement (see below), resulting in substantial financial penalties, and jeopardize viability of the Project.

r knowledge of plugging potential and of operational conditions that avoid plugging may permit loosening of overly restrictive process control requirements. This would reduce waste volume and programmatic time and costs.

pletion of the leach-testing strategy supports retrieval sequence development and broadens the technical foundation that is needed for planning Phase 2. This will result in better separations at less cost, producing a lower volume of final immobilized waste form.

	A significant waste volume reduction and concomitant cost avoidance is expected during Phase 1 if the sludge washing process for aluminum can be optimized. Removal of aluminum will produce additional savings during Phase 2, but a much greater cost avoidance is expected if chromium can be removed effectively from the sludge in Phase 2.	
17 *	Potential Cost Savings: Pluggage avoidance: \$2M/yr Canister cost avoidance: \$6,000 M	
18 *	Potential Cost Savings Narrative: The pluggage avoidance estimate is based on an estimate of two plugs per year and an estimate of \$1M to remove the plug and recover from its effects. This does not include additional costs that that could be incurred to schedule slippage. The number of plugs that occur each year is extremely variable, depending on the types of operations being conducted and the frequency of each (experience factor).	
	The canister cost avoidance is difficult to calculate because the leachability of chromium may be in error by a factor of two. The estimate given is based on the current estimate that HLW will fill 12,500 canisters, and that, if all the chromium could be removed, about 3000 canisters could be avoided. The cost of making and disposing of a single canister is estimated to be \$2M. Despite the vagaries of this estimate, the possible cost savings are certainly large.	
**	Technical Basis: This effort will provide a basis for feed delivery and treatment operations during Phase 1B. The current state of knowledge is insufficient to predict, in all cases, whether planned transfers are feasible, whether leaching will achieve waste minimization goals, or whether unplanned solids precipitation may occur during processing in the waste treatment plant.	
19	Cultural/Stakeholder Basis: Long-term disposal of the high-level wastes stored in Hanford's underground tanks is a national priority. The DOE has a legal agreement (the Tri-Party Agreement) with the Environmental Protection Agency and the State of Washington Department of Ecology to dispose of the waste according to a stated schedule. Native American tribal interests and a number of public interest groups monitor adherence to this agreement. Program delays due to inability to retrieve and deliver waste feeds containing solids may violate the Tri-Party Agreement.	
20	<i>Environment, Safety, and Health Basis:</i> Without this work, plugging of lines is more likely. Recovery from pipe plugging incidents normally involves exposure of personnel to ionizing radiation beyond planned levels.	
21	Regulatory Drivers: Tri-Party Agreement	
22*	<i>Milestones</i> : Supports technical basis of TPA milestone M-45-02 "Submit annual updates to SST retrieval sequence document,", due at the end of each fiscal year.	
23*	Material Streams: Hanford high-level defense waste	
24*	TSD System: Double Shell Tank System and Single Shell Tank System	
25	<i>Major Contaminants</i> : Fission products, actinides, nitrate. Pu-238, 239, 240, 241; AM-241; U-238; C-14; Ni-59/63; Nb-94; Tc-99; I-129;Cm-242; Sr-90; Cs-137; Sn-126; Se-79; chromium; nitrate; nitrite; complexants (EDTA/HEDTA)	
26	Contaminated Media: N/A. This project addresses wastes in engineered containment.	
27	Volume/Size of Contaminated Media: There are 54 million gallons (204 dam³) of Hanford sludge and saltcake wastes stored in underground tanks. [Ref: B. M. Hanlon, "Waste Tank Summary Report for Month Ending July 31, 2001," HNF-EP-0182, Rev. 160, (CH2M HILL Hanford Group, Inc., Richland, WA, September 2001).]	
28 *	Earliest Date Required: FY 2002	
29 *	Latest Date Required: 2020	
Baseline Technology Information		
30	Baseline Technology/Process: Process testing with actual waste samples is now used to obtain needed data: these tests are not extensive and do not indicate quantitatively how leachability may be affected by	

	process variable, such as temperature and time. The ESP software is used in conjunction with the process tests; ESP has been only partially validated with actual waste solubility data. ESP does not provide physical property data.
	Technology Insertion Point(s): N/A
31	<i>Life-Cycle Cost Using Baseline</i> : Activities 150.B22, "Maintain the Operations & Utilization Plan," and 120.025, "Maintain WFD Technical Basis," will make use of the data provided under this site need. Funds allocated for these activities are \$1.2M in FY2002, about the same each year through FY2018. Several activities provide funding for limited laboratory characterization of sludge wastes. Activities 160.S10, 120.B20, and 120.R10 provide \$0.6M in FY2002, and similar activities provide \$1.1M in FY2003, \$0.8M in FY2004, and \$0.4M in FY2005. Life Cycle Costs related to Sludge retrieval and transfer to the treatment plant are estimated at \$4-8 Billion. This includes equipment, operations, maintenance and infrastructure upgrades over time, but does not include "closure".
32	Uncertainty on Baseline Life-Cycle Cost: Unknown
33	Completion Date Using Baseline: Activities, "Maintain the Operations & Utilization Plan," and "Maintain WFD Technical Basis," are planned to continue throughout the life of the project. The laboratory characterization activities will complete in FY2006. The RPP is scheduled to complete post 2020.
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